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Epitaxial Growth and Dopant Incorporation in Diamond:
Surface/Interface Studies based on Synchrotron Radiation

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Max Yoder
Office of Naval Research

B.B. Pate, I. Lindau and W.E. Spicer

Stanford Synchrotron Radiation Laboratory
Stanford University

P.O. Box 4349
Stanford, California 94309

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<p>We summarize our experimental studies of the microscopic structure of diamond. We have used Angle Resolved Photo-Electron Spectroscopy (ARPES) to study the electronic structure of the reconstructed (111) 2×1 surface and the clean (110) surface which might be topologically similar. We confirm the Pandey π-bonded structure of the (111) 2×1 surface and find that the clean (110) surface is distinct from the ideal structure. Extended x-ray absorption fine structure (EXAFS) measurements of diamond and graphite demonstrate the applicability of the "standard" spherical-wave EXAFS analysis in low Z (atomic number) systems such as diamond. This work provides the basis for future Surface EXAFS (SEXAFS) measurements of the local structure of dopants and impurities in/on diamond. Collaboration with M. Geis at MIT Lincoln Labs resulted in an electrical measurement study of the silicon oxide-NEA (negative electron affinity) diamond interface. We showed that there is no electrostatic barrier to electron emission into SiO_2 from the diamond conduction band.</p>					
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I. Technical Summary

When a diamond crystallite grows from the vapor phase, there are a series of steps which occur in order to properly insert the new carbon atoms into the diamond lattice. Similarly, when impurities are incorporated during growth, certain steps must occur to result in a substitutional dopant. Furthermore, there appear to be "catalytic" effects due to surface impurities which modify (often with increased growth rates) the homo-epitaxy of diamond. Our efforts pursued the use of synchrotron radiation techniques to probe the local atomic and electronic structure of diamond surfaces and interfaces.

During the course of this contract, we have 1) studied structural aspects of the principle surfaces of diamond, 2) developed needed analytical and experimental tools (low atomic number EXAFS) for the study of local surface structure on the atomistic level, 3) applied synchrotron radiation techniques (NEXAFS) to the study of bond purity in diamond, and 4) explored unique devices made possible by the novel negative electron affinity of diamond (111):H.

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II. Summary of Work Accomplished

A. Surface State Dispersion of the Intrinsic Diamond (111) and (110) Surface

An intriguing similarity in structure between the grossly reconstructed π -bonded chain reconstruction of the (111) surface and the ideal truncated (110) surface is apparent. One might argue from purely empirical reasoning that a slight relaxation of the ideal (110) surface is all that might be needed to stabilize the clean (110) surface. This is in contrast to the severe reconstruction of the clean (111) surface. If true, this would imply that drastic rehybridization of the (110) surface could be avoided, and therefore an atomic-hydrogen-free diamond growth process might be possible on diamond (110). Such a process might open the way to 1) faster diamond growth rates and 2) lower temperature diamond growth (since on other principal surfaces hydrogen must be removed before, or during, addition of a carbon atom and since much data points to the belief that thermal activation of the surface is required to remove hydrogen and thereby promote diamond growth. With this thought in mind, we made comparative measurements of the electronic band structure of the clean (111) and (110) diamond surfaces.

We have measured the Γ (zone center) \rightarrow K (corner point) dispersion of the filled electronic surface states at the diamond (110) surface to the $\Gamma \rightarrow$ K surface state dispersion of the (111) surface. In both cases we find bands which are relatively flat near gamma, and disperse upwards as we approach the zone boundary. We find that the overall width of surface state dispersion on each of the two surfaces is, within the accuracy of our data, identical at 1.7 eV. However the k dependence of the two dispersion curves differ. These results find that the clean (110) surface is not simply a

relaxed ideal truncated bulk lattice.

Further details of this study can be found in our publication:

B. B. Pate, J. C. Hwang, J. Woicik, J. Wu, I. Lindau, and W. E. Spicer, "Electronic structure of the diamond surface; surface state dispersion of diamond (111) and (110)," Science and Technology of New Diamond, edited by S. Saito, O. Fukunaga, and M. Yoshikawa, pp. 345-350. (KTK Scientific Publishers/Terra Scientific Publishing Company, 1990).

B. Extended x-ray-absorption fine-structure studies of diamond and graphite

Our approach has been to apply multiple surface sensitive techniques in order to form a complete and consistent understanding. Most challenging, and potentially most important, is the use of the technique of EXAFS (Extended x-ray absorption fine structure) analysis to directly extract structural parameters (bond length and atom coordination) of low atomic number impurities on/in diamond. Our program challenged the simple (eg plane wave) EXAFS theory and standard experimental technique by applying the technique to first row elements. Included among our accomplishments is the demonstration of the validity of this technique when applied to low atomic number (eg. carbon) systems.

We have recorded the extended x-ray-absorption fine structure (EXAFS) above the carbon K edge for diamond and highly oriented crystalline graphite using 250-800 eV synchrotron radiation. The spectra are used to test phase and amplitude transferability of the C-C EXAFS signal between the two bonding forms of carbon. We find excellent phaseshift transferability with errors in distances less than 0.01 Å. Amplitude transferability is worse but better than 20%. Implications of our results for structural determinations of C-C bonds in molecules and solids are discussed.

Further details of this study can be found in our publication:

G. Comelli, J. Stohr, and B.B. Pate, "Extended x-ray absorption fine structure studies of diamond and graphite," Phys Rev B37, 4383 (1988).

C. Capacitance-Voltage Measurements on Metal-SiO₂-Diamond Structures

Fabricated with (100)- and (111)-Oriented Substrates

A unique property of the diamond (111):H surface is that it has a negative electron affinity, which means that there is no electrostatic barrier to electron emission from the diamond conduction band. In this effort, Metal-SiO₂-diamond structures were fabricated using (100)- or (111)-oriented substrates of type IIb natural diamond, which is a p-type semiconductor. The SiO₂-diamond interface was electrically characterized by measuring the capacitance between the metal electrode and the diamond substrate as a function of bias voltage. Capacitance-voltage (C-V) characteristics were measured for various SiO₂ thicknesses and substrate temperatures, with and without

exposure to ultraviolet light.

When biased into depletion, the metal-SiO₂-diamond structures showed no indication of minority-carrier electrons accumulating at the SiO₂-diamond interface. This is believed to be due to the low electron generation rate in the diamond and the small barrier for electrons to enter SiO₂ from the diamond conduction band. For (100)-oriented substrates, the capacitance varied substantially with temperature near accumulation, but showed no significant change in depletion. Exposure of (100)-oriented substrates to ultraviolet light, which generates conduction band electrons in diamond, resulted in the accumulation of electrons at the SiO₂-diamond interface, which affected the C-V measurements. On the other hand, this light had no substantial effect on the (111)-oriented substrates, because of the absence of a barrier for electrons to enter the SiO₂. On the other hand, this light had no substantial effect on the (111) oriented substrates, because of the absence of a barrier for electrons to enter the SiO₂. From the C-V measurements, the conduction band of diamond was determined to be 2.3 eV below and .7 eV above vacuum level for (100) and (111) oriented substrates, respectively. Metal-SiO₂-diamond structures on (100) oriented substrates appear to be acceptable for depletion-mode metal-oxide-semiconductor field-effect transistors (FET's), while (111)-oriented substrates may be used as robust cold cathodes.

Further details of this study can be found in our publication:

M. W. Geis, J. A. Gregory, and B. B. Pate, "Capacitance-voltage measurements on metal SiO₂ -diamond structures fabricated with (100)- and (111)-oriented substrates," IEEE Transactions on Electron Devices 38, 619-626 (1991).

D. Characterization of diamond materials with Near-Edge-Xray-Absorption-Fine-Structure (NEXAFS).

Comparative bond-purity studies of man-made carbon films (plus graphite and natural diamond) have been made using the Near-Edge-Xray-Absorption-Fine-Structure (NEXAFS) technique. Analysis of the xray absorption structure reveals bonding character through the dependence of absorption on the available empty states during the absorption excitation of the carbon 1s level into the conduction band. In particular, the carbon 1s→ π^* absorption feature, was used to characterize the amount of defect bonding (π -bonding) in the films. Note that diamond is characterized by single C-C bonds, sp³ hybridization, and tetrahedral bonding, while other forms of crystalline carbon (eg. graphite and carbynes) are characterized by multiple bonds between carbons, non-hybridized p-orbitals (eg π -bonding), and a planar or linear structure. In the non-diamond forms of carbon, the non-hybridized p-orbitals split into filled bonding orbitals (the π -band) and empty anti-bonding orbitals (the π^* -band). In preliminary work we have found that carbon films provided by Dr. A. Nyaiesh of the Stanford Linear Accelerator Center, are disordered with substantial π -bonding (see

figure, diamond-like carbon), while certain films provided by Dr. M. Pinneo of the Crystallume company (Stanford, California) show nearly identical structure to our natural diamond substrate (see figure, diamond film #1), with no detectable $\pi \rightarrow \pi^*$ absorption feature (above our background). With this data, we can make a quantitative estimate of π -bonding in the film to be no more than several percent of the total number of bonds in the film. Also demonstrated was the effect that processing parameters have on the bond purity of the diamond film, as only a small change in methane dilution in the growth reactor caused a substantial ($\sim 10\%$) increase in the π -bonding signature.

Further details of this study can be found in our report:

B.B. Pate, 1st year Annual Letter Report (June 1988), contract N00014-87-K-0262, "Epitaxial Growth and Dopant Incorporation in Diamond; Surface/Interface Studies based on Synchrotron Radiation."

III. Publications and Presentations of this work

A. Papers Published in refereed Journals

G. Comelli, J. Stohr, and B.B. Pate, "Extended x-ray absorption fine structure studies of diamond and graphite," *Phys Rev B* 37, 4383 (1988).

B. B. Pate, J. C. Hwang, J. Woicik, J. Wu, I. Lindau, and W. E. Spicer, "Electronic structure of the diamond surface; surface state dispersion of diamond (111) and (110)," *Science and Technology of New Diamond*, edited by S. Saito, O. Fukunaga, and M. Yoshikawa, pp. 345-350. (KTK Scientific Publishers/Terra Scientific Publishing Company, 1990).

M. W. Geis, J. A. Gregory, and B. B. Pate, "Capacitance-voltage measurements on metal SiO₂-diamond structures fabricated with (100)- and (111)-oriented substrates," *IEEE Transactions on Electron Devices* 38, 619-626 (1991).

B. Invited Presentations

B.B. Pate, "Diamond at Stanford University," presentation to the Advisory Group on Electronic Materials, U.S. Department of Defense, Durham, North Carolina (December, 1987).

B.B. Pate, "Characterization of Diamond with Synchrotron Radiation," invited paper at the International Symposium on the Characterization of Diamond, Tsukuba, Japan (October 1988).

B.B. Pate, "Diamond Surface/Interface Science: The Role of Surface Structure in Low Pressure Diamond Growth," Stanford University Short Course on Diamond Films, Stanford, California, February 1, 1989.

B.B. Pate, "Atomic And Electronic Structure Of The Diamond Surface," invited

seminar to the Physics Department, Washington State University. (February, 1989).

B.B. Pate, "Atomic And Electronic Structure Of The Diamond Surface," invited seminar to the Physics Department, Kansas State University. (March, 1989).

B.B. Pate, "Physical and Chemical Properties of the Diamond Surface," invited seminar at the Los Alamos National Laboratory (February, 1990).

B.B. Pate, "Physical and Chemical Properties of the Diamond Surface," invited presentation at the March meeting of the American Physical Society (Los Angeles, 1990).

C. Contributed Presentations at Topical or Scientific/Technical Society Conferences

B.B. Pate, "Hybridization States of the Diamond Surface," presented at the Diamond Technology Workshop, M.I.T. Lincoln Labs (February , 1987).

B.B. Pate, "Synchrotron Radiation Studies of Diamond," presented at the 2nd annual symposium of the Diamond Technology Initiative, Durham, North Carolina (July, 1987).

B.B. Pate, J. Hwang, J.C. Woicik, J. Wu, I. Lindau, and W.E. Spicer, "Surface State Dispersion of Intrinsic Diamond; the (111) and (110) surface," presented at the 15th annual conference on the Physics and Chemistry of Semiconductor Interfaces, PCSI-15, Asilomar, California, February 1988.

B.B. Pate, J. Hwang, J.C. Woicik, J. Wu, I. Lindau, and W.E. Spicer, "Electronic Band Structure of the Intrinsic Diamond (111) and (110) Surface," presented at the Spring meeting of Materials Research Society, Reno, Nevada, April 1988.

B.B. Pate, J. Hwang, J.C. Woicik, J. Wu, I. Lindau, and W.E. Spicer, "Surface Band Structure of Diamond (111) and (110)," presented at the 3rd annual symposium of the Diamond Technology Initiative, Washington, D.C., July 1988).

B.B. Pate, G. Comelli, and J. Stohr, "EXAFS studies of Diamond and Graphite," presented at the 3rd annual symposium of the Diamond Technology Initiative, Washington, D.C., July 1988.

B.B. Pate, J. Hwang, J.C. Woicik, J. Wu, I. Lindau, and W.E. Spicer, "Electronic Structure of Diamond Surfaces," presented at the First International Conference on the New Diamond Science and Technology, Tokyo, Japan (October 1988).

B.B. Pate, J. Hwang, J.C. Woicik, J. Wu, I. Lindau, and W.E. Spicer, "Electronic Structure of Diamond Surfaces," Stanford University Short Course on Diamond Films, Stanford, California, February 1, 1989.

B.B. Pate, "The Electronic and Atomic Structure of Diamond Surfaces," 19th Biennial Conference on Carbon, University Park, Pennsylvania (June 1989).

D. Printed technical reports & non-refereed papers published.

B.B. Pate, J. Hwang, J.C. Woicik, J. Wu, I. Lindau, and W.E. Spicer, "Electronic Band Structure of the Intrinsic Diamond (111) and (110) Surface," in (Extended Abstracts) Diamond and Diamond-Like Materials Synthesis, ed. G.H. Johnson, A.R. Badzian, and M.W. Geis, Materials Research Society, vol. EA-15, p67, 1988.

B.B. Pate, "The Electronic and Atomic Structure of Diamond Surfaces," in Proceedings of the 19th Biennial Conference on Carbon, University Park, Pennsylvania, (June 1989).

B.B. Pate, 1st year Annual Letter Report (June 1988), contract N00014-87-K-0262, "Epitaxial Growth and Dopant Incorporation in Diamond; Surface/Interface Studies based on Synchrotron Radiation."

B.B. Pate, 2nd year Annual Letter Report (June 1989), contract N00014-87-K-0262, "Epitaxial Growth and Dopant Incorporation in Diamond; Surface/Interface Studies based on Synchrotron Radiation."